NATIONAL BUREAU OF STANDARDS May 1966

Technical News Bulletin

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TECHNOLOGY & SCIENCE

IT IS THEREFORE THE UNANIMOUS OPINION OF YOUR
COMMITTEE THAT NO MORE ESSENTIAL AID COULD BE
GIVEN TO MANUFACTURING, COMMERCE, THE MAKERS
OF SCIENTIFIC APPARATUS, THE SCIENTIFIC WORK
OF THE GOVERNMENT OF SCHOOLS, COLLEGES AND
UNIVERSITIES THAN BY THE ESTABLISHMENT OF THE
INSTITUTION PROPOSED IN THIS BILL."

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

Technical News Bulletin

MAY 1966/VOL. 50, NO. 5/ISSUED MONTHLY

U.S. DEPARTMENT OF COMMERCE
John T. Connor, Secretary

NATIONAL BUREAU OF STANDARDS
A. V. Astin, Director

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COVER

The Nation's two key measurement standards were received at the new NBS site in Gaithersburg, Md., by (from left) Dr. J. Herbert Hollomon, Assistant Secretary of Commerce for Science and Technology; Dr. Donald Hornig, the President's Science Adviser; Dr. A. V. Astin, NBS Director; and A. G. McNish, Chief, NBS Metrology Division. *(See page 78.)*

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The National Bureau of Standards serves as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. For this purpose, the Bureau is organized into three institutes—

- The Institute for Basic Standards
- The Institute for Materials Research
- The Institute for Applied Technology

The TECHNICAL NEWS BULLETIN is published to keep science and industry informed regarding the technical programs, accomplishments, and activities of all three institutes.

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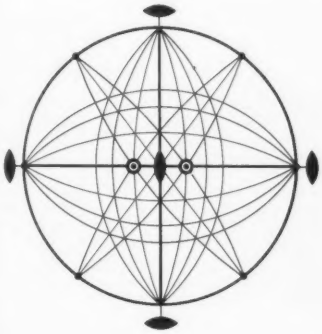
NBS Standard No. 725, a platelet of sodium nitroprusside, is shown in its protective envelope next to a large single crystal of the material from which the standards are cut.



Standard Reference Material for

MÖSSBAUER SPECTROSCOPY

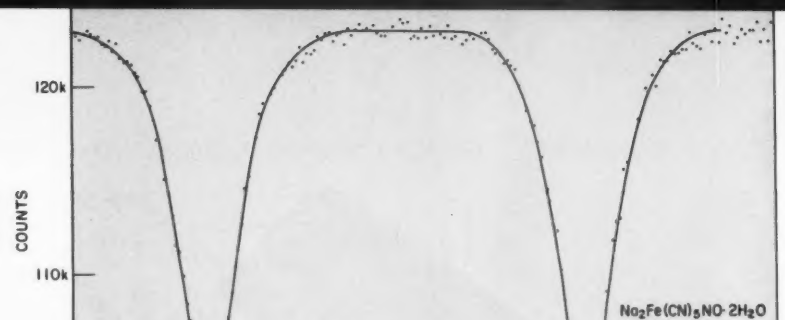
A standard reference material for Mössbauer spectroscopy has recently been made available by the NBS Office of Standard Reference Materials.[1] NBS Standard No. 725, sodium nitroprusside, is issued as a standard Mössbauer absorber.

Mössbauer spectroscopy has become an important tool for determining the structural properties of compounds and materials. Chemical compounds can be characterized by their Mössbauer parameters, the chemical shift and quadrupole splitting. The measurement of the chemical shift depends on the particular source used, and its preparation. This fact has caused considerable confusion, and makes it impossible to compare data from various laboratories.

The difference in chemical shift between two absorbers may be measured when a single source is used. When two sources are used, however, the difference in chemical shift between two absorbers cannot be measured accurately. In fact, the use of two supposedly identical sources with a single absorber produces significant differences in the chemical shift even when great care is exercised to maintain identical chemical environment.

To eliminate this problem, scientists in the Mössbauer group, headed by

continued



The Mössbauer spectrum of NBS Standard No. 725, sodium nitroprusside, shows two peaks, the midpoint of which is arbitrarily designated as zero chemical shift.

SPECTROSCOPY *continued*

James R. DeVoe and Jon J. Spijkerman, in the Analytical Chemistry Division of the Institute for Materials Research, have recently proposed the use of a standard absorber in Mössbauer spectroscopy. The use of such a standard would permit the reporting of data on the chemical shift as the difference between the chemical shift of the compound and that of the standard. This would be called the differential chemical shift.

To facilitate this proposal, the new standard reference material was recently prepared and certified. NBS Standard No. 725 is a single crystal of disodium pentacyanonitrosoferrate dihydrate, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$, commonly known as sodium nitroprusside. In its properly oriented single-crystal form this iron compound has all of the necessary properties for a standard of chemical shift.

When placed in a Mössbauer spectrometer with the gamma-ray vector perpendicular, within ± 2 degrees of arc, to the plane of the platelet, this crystal produces a spectrum in which two peaks are observed. These peaks are the result of an electric quadrupole splitting of the 14.4 keV excited state in the iron–57 of the absorber.

The midpoint of the two peaks, which is the chemical shift of the standard, is arbitrarily designated as zero chemical shift. For any source the chemical shift of a compound is measured with respect to this zero point and reported as the differential chemical shift.

Sodium nitroprusside was selected as the standard material because of its chemical stability, low temperature coefficient, narrow line width, and because it has a doublet. The standard is issued as a single crystal because the reproducibility of the spectrum obtained is maximized in that form.

This high reproducibility permits the standard to be measured with the Bureau's optical interferometric Mössbauer spectrometer which has an accuracy within 0.0001 cm/s. Thus, the standard may also be used to calibrate the velocity scale of Mössbauer spectrometers.

This standard may be purchased from the NBS Office of Standard Reference Materials for $150.

[1] For a list of NBS standards, see **Standard Reference Materials: Catalog and Price List of Standard Materials Issued by the National Bureau of Standards**, NBS Misc. Publ. 260, available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402, for 45 cents.

TENTH SCINTILLATION AND SEMICONDUCTOR COUNTER SYMPOSIUM

Over 800 engineers and scientists from North America and Europe attended the 10th Scintillation and Semiconductor Counter Symposium in Washington, D.C., from March 2 to March 4, 1966. The Symposium was established in 1948 to bring about an interdisciplinary approach to discussions of particle detector design and use. Held at 2-year intervals, the meeting provides an opportunity for both the designers and users of particle detectors to review current techniques of particle detection, to exchange ideas and information, and to outline future needs. The meeting is sponsored jointly by the National Bureau of Standards, the Atomic Energy Commission, and the Institute of Electrical and Electronic Engineers.

The Symposium consisted of six sessions: Detector Applications, Scintillators and Tubes, Semiconductor Detectors (two sessions), Circuits, and Systems. At a dinner meeting on March 2, Dr. Herbert Friedman of the U.S. Naval Research Laboratory spoke on "Cosmic X-Rays and Gamma Rays." The Symposium papers were concerned with scintillation and semiconductor detectors for the detection and measurement of ionizing radiation and with the circuits and instruments required for these detectors. New developments in the field were described as well as techniques for readout of the massive spark chambers that have been constructed in recent years for use with multimillion-volt particle accelerators.

The proceedings of the Symposium will be published in the fall of 1966 in the Transactions of IEEE.

A Laboratory Study

MINIMUM VENTING FOR PLUMBING SYSTEMS

A recent study of an experimental plumbing system at the NBS Institute for Applied Technology using clear-water loadings showed satisfactory performance of a single-story, single-bath plumbing system with vents much smaller in diameter than those presently specified by plumbing codes. However, the investigators cautioned against any changes in the code sizes for vents at this time, pending further investigation to take account of field conditions not covered in the study.

The study, sponsored by the National Association of Home Builders and conducted by R. W. Beausoliel and R. S. Wyly, showed that the use of vents as small as ½-in. inside diameter (I.D.) did not seriously impair hydraulic or pneumatic operation of the one-story laboratory test system. It has been estimated that this could reduce the cost of a typical system by $25 to $50. The use of manifold-type vent terminals, such as used in the study, extending horizontally through gables or exterior walls, might provide additional savings for some systems by eliminating costly roof penetrations and flashings. Since possibly as many as 300,000 single-story residential-type systems are reported to be constructed annually in the United States, a total annual national savings of over $10 million might, therefore, be expected. Both the potential savings from the use of small vents and certain unresolved questions as to performance that might be expected under field conditions appear to be of such importance as to justify further investigation and field trials.

Venting has long been considered necessary to protect fixture trap seals from pneumatic pressure fluctuations great enough to impair the seals' usefulness. Excessive fluctuation in system pressure resulting from inadequate or blocked venting may cause excessive loss of the water seal into the drainage system or a backup of waste water into the plumbing fixture, neither of which can be tolerated.

Air Demand Values

Published air demand values widely used as a guide in preparing vent-sizing tables in plumbing codes originated from earlier laboratory experimentation with multi-story systems subjected to clear-water loadings.[1, 2] Air demand was determined for stack vent pressures closely approaching atmospheric. This information has proved useful in establishing vent-size requirements. However, it may have resulted in the specification of vent sizes larger than necessary for one-story systems, since air demand is reduced both by shortening stack length and by allowing the stack vent pressure to deviate somewhat from atmospheric within the range ±1 in. of water, as allowed by codes. While some recent work relating to effects of solids and detergents in drainage loads on trap-seal retention has been reported, evidently no measurements were made of volume rate of air demand.[3, 4, 5, 6]

As one result of a previous study of the hydraulics of horizontal drains,[7] adequate sizing of drainage piping and the use of selected types of fittings were suggested as possible means to reduce air demand, and hence the size or number of vents, without overall loss of system efficiency. Further study of these measures was recommended.

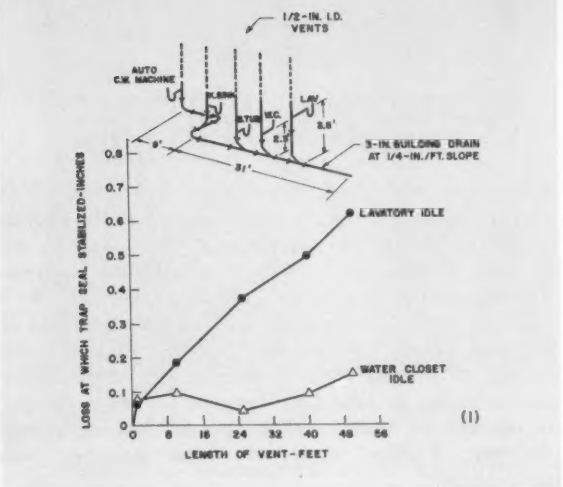
Experimental System

In the present study, the experimental system consisted of a simple, single-bath test plumbing system with minimum kitchen and laundry facilities designed for a one-story single-family house without a basement. Initially, the test system was vented with a 1½-in. I.D. stack vent for each fixture except the water closet, which had a 3-in. I.D. vent. These sizes are customary under the provisions of many plumbing codes. Tests with various hydraulic loadings indicated altogether satisfactory performance of the trap seals, as might have been expected.

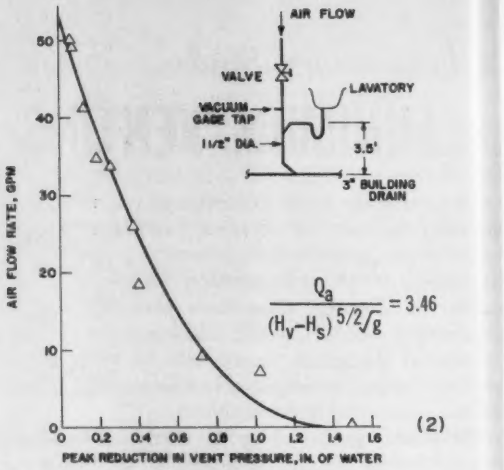
Next, peak air demands for several fixtures discharged individually were determined as a function of stack vent vacuum which was independently controlled by partial closure of valves in the vents to simulate longer or smaller vents. These measurements showed that substantial reductions of the vent diameters or extensions of the vent lengths could be made in the test system without violating the codes' vent pressure requirements. The peak volume rate of air flow (air demand) was computed as the product of the cross sectional area of the vent and the peak air speed. The air speed was determined by a "heat pulse" technique in which an oscillograph record was obtained of the responses of two thermocouples placed in tandem in the vent when sensing the passage of successive slugs of air heated by "pulsing" (frequency of approximately 1 cycle per second) an electric heater placed near the vent terminal. Calibration indicated an overall accuracy of within ±7 percent in the air-speed measurements. The vacuum was measured in the stack vent a few inches above the connection of the fixture drain to the soil or waste stack, using a sensitive strain-gage type of differential pressure transducer, and was recorded on a third channel of the oscillograph.

Small, flexible plastic tubing was then substituted for the conventional vent piping throughout the test system,

continued



Stabilized trap-seal performance for lavatory and water closet traps as a function of length of ½ in. I.D. individual fixture vents. All fixtures were discharged simultaneously except the one indicated as idle. Plotted points represent maximum seal loss for indicated load; seal loss remained at this value for four successive load applications without seal replenishment.



Peak air flow rate, Q_a, in 1½ in. vent during discharge of lavatory into 3.5 ft, 1½ in. dia. waste stack, shown as function of minimum vent pressure, H_v. Curve computed from the equation shown in the figure. H_s=minimum vent pressure with closed vent (−1.50 in.), H_v=minimum vent pressure with stack vent partially or fully open, g=32.2 ft/sec.²

PLUMBING SYSTEMS *continued*

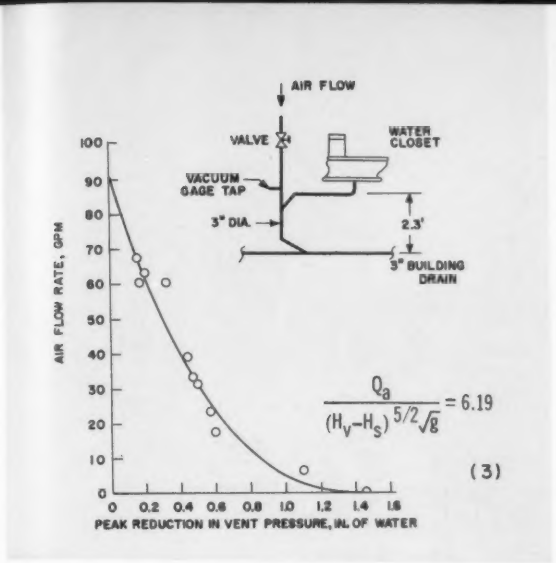
beginning well above the flood-rim levels of the fixtures. The tubing vents were connected to a horizontal vent manifold (a 4-ft length of 2-in I.D. pipe) through adaptors along its length. Such a manifold could be installed to penetrate a gable or an exterior wall. The main advantages of such a vent manifold would be: (1) convenience in connecting individual vents to a single terminal fitting in a single location, and (2) elimination of costly roof penetrations and flashings by use of a single outlet through the gable or exterior wall. This system was tested with both individual and multiple-fixture loadings. Experimental results showed that it performed satisfactorily without failure or excessive loss of the trap seals, even under very heavy hydraulic loadings.

Experimental Results

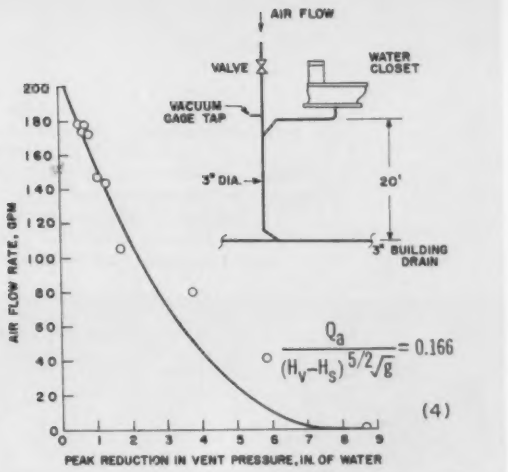
Stabilized trap seal loss* was plotted as a function of vent length for a simultaneous discharge of all fixtures except the lavatory and water closet. Similar plots were obtained for multiple fixture loadings involving other fixture combinations and operating sequences. The seals of both idle and operating fixtures were satisfactorily maintained** under various severe loadings, even with a 50-ft, ½-in. I.D. vent for each fixture.

In the tests of various individual fixtures, peak air flow rate was plotted as a function of peak vacuum generated in the vent by the fixture discharge. A valve was used to simulate the effects of various combinations of vent diameters and lengths. As the peak vacuum in the stack vent was increased, the required rate of air flow in the vent (air demand) was substantially reduced. For example, air demand was substantially less for a vacuum of ½-in. (water-gage pressure) below atmospheric than for a negligible vacuum. The reduction in demand at a 1-in. vacuum was still more striking. Air demand values that have been utilized by the code writers in specifying vent sizes were based on data for a negligible vacuum in the stack vent despite the fact that codes allow a vent pressure range of ±1 in. of water. Therefore, by virtue of the fact that air demand on vents of one-story systems at allowable vent pressure is actually less than currently assumed, some reduction in usual vent diameter or extension of usual vent length seems justified. A vent can be readily sized for any given vent pressure if the air demand for the vent is known for this pressure.

A comparison of data for tall and short soil stacks, vented only by the stack vent (soil vent), showed that air demand for a 20-ft water closet soil stack was much greater than that for a short 2.3-ft soil stack. The tall system required a peak air demand of approximately 160 gpm (10.1 liters per second) so as not to exceed a 1-in. water gage vacuum in the vent, while for the same vent pressure limitation, the short stack demanded less than 10 gpm (0.63 liters per second) peak air flow. Actually, had venting been provided at each story height of the tall stack, it is quite likely that the air demand in the vent at each level would have been appreciably less than that determined with venting only at the top of the stack.



Peak air flow rate, Q_a, in 1½ in. vent during discharge of conventional flush-tank water closet into 2.3 ft, 3-in. dia, soil stack, shown as a function of minimum vent pressure, H_v. Curve computed from the equation shown in the figure. H_s=minimum vent pressure with closed vent (−1.46 in.), H_v=minimum vent pressure with stack vent partially or fully open, g=32.2 ft/sec.²



Peak air flow rate, Q_a, in 2-in. vent during discharge of conventional flush-tank water closet into 20-ft, 3-in. dia. soil stack without venting at intermediate level, shown as a function of minimum vent pressure, H_v. Curve computed from the equation shown in the figure. H_s=minimum vent pressure with closed vent (−8.73 in.), H_v=minimum vent pressure with stack vent partially or fully open, g=32.2 ft/sec.²

High-rise laboratory facilities and further data are needed to satisfactorily establish air demand in multistory sanitary drainage systems.

Further Study Needed

Further performance data must be acquired from laboratory experimentation and field trials with small vents for one- and two-story systems to establish whether plumbing codes can be safely modified to allow such venting. Among other things, laboratory experiments should be made with representative solids and detergents in certain test loads, since such materials may affect required vent sizes in some instances. Solids and detergents were not used in the tests described here because of difficulties in standardizing such test loads and in obtaining reproducibility. Because of these difficulties, it was considered preferable first to explore performance of a system with clear-water loadings over a relatively wide range of conditions, and to incorporate other matter in the loadings in later test work as suggested by the results of the clear-water tests.

Field trial should include evaluation of any effects of moisture and solids accumulation in small vents, including effects of frost closure where this might be a pertinent consideration.[8] These factors are frequently cited in support of the use of vents at least 1¼ in. in diameter. Field performance of air relief valves could also be studied.

Recent tests and field trials conducted abroad have shown that pneumatic pressure disturbances in a drainage system can be reduced by enlarging the drainage piping, or in some cases by using special new types of fittings at the junctions of the drainage stack and the horizontal fixture branches. This work has been directed particularly to multistory plumbing. Since these findings suggest that it might be technically feasible to eliminate some vents under certain conditions, it now becomes important to evaluate the overall value of such measures in relation to American plumbing practice, from both technical and practical standpoints.

*The stabilized trap seal loss is that at which no further reduction in seal depth is evident with repeated applications of selected fixture discharge patterns. The patterns of discharge employed in these tests were considered extremely severe in regard to number of fixtures in concurrent operation, and unlikely to be encountered in normal use of the system.

**Trap seals were considered to be satisfactorily maintained if they stabilized at a seal loss of less than 1 in. when subjected to repeated applications of the indicated test load.

[1] **Capacities of Stacks in Sanitary Drainage Systems for Buildings**, by Robert S. Wyly and Herbert N. Eaton, NBS Monograph 31 (July 1961). Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402, for 35 cents.

[2] **Report on Hydraulics and Pneumatics of Plumbing Drainage Systems**, University of Iowa Studies in Engineering, Bulletin 10 (1937).

[3] **Standard Plumbing Engineering Design**, by Louis S. Nielsen (1963). Available from McGraw-Hill Book Company, New York, N.Y.

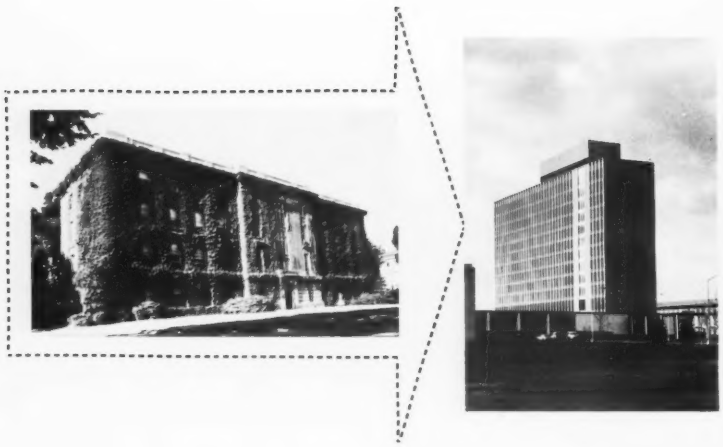
[4] **Santa Fe Springs PHC Contractor Testing Drainage Systems for Size**, California Plumbing Contractor (March 1965).

[5] **Elmer Renz Dissects Copper Table**, California Plumbing Contractor (April 1965).

[6] **Over the Editor's Desk—More on Copper Table**, California Plumbing Contractor (May 1965).

[7] **Investigation of the Hydraulics of Horizontal Drains in Plumbing Systems**, by Robert S. Wyly, NBS Monograph 86 (December 1964). Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402, for 35 cents.

[8] **Frost Closure of Roof Vents in Plumbing Systems**, by Herbert N. Eaton and Robert S. Wyly, NBS BMS 142 (October 1954).



National Standards Transferred on NBS 65TH BR

Secretary of Commerce John T. Connor participated in a ceremony on March 3, 1966, in which the nation's two key measurement standards were removed from a vault they had occupied for 60 years at the Bureau's Washington, D.C., site and were taken to their new home in Gaithersburg, Md. The day of the transfer was chosen to coincide with the 65th anniversary of the founding of the National Bureau of Standards.

At the Gaithersburg site to witness the arrival of the standards—a platinum-iridium meter bar and a kilogram weight—were Dr. Donald Hornig (Science Adviser to President Johnson), Dr. J. Herbert Hollomon (Assistant Secretary of Commerce for Science and Technology), and Dr. Allen V. Astin (NBS Director).

Supervising the actual physical transfer of the two standards were Alvin G. McNish, Chief of the NBS Metrology Division; Paul Pontius, Chief of the Mass and Volume Section; and Theodore Young, Chief of the Length Section.

The kilogram and meter bar represent the basis for virtually the entire system of measurement used in the United States. The kilogram is the national standard of mass, and any related measurements, whether the weighing out of a tiny bit of medicine at the pharmacy or the weighing of a loaded freight car, are made in terms defined by this one weight. The meter bar was the national standard for length measurements for 70 years. In 1960, it was replaced by a new and more accurate standard based on a wavelength of light from a krypton-86 lamp. However, the bar is still a most valued measuring tool.

The meter bar and kilogram were brought to this country

A. G. McNish carries a platinum-iridium meter bar into the administration building at the Bureau's new Gaithersburg (Md.) laboratories. There it was placed in a new standards vault, along with a duplicate meter bar and two platinum-iridium one-kilogram weights, one of which is the Nation's standard of mass.

Secretary of Commerce John T. Connor stands behind case containing the meter bar and kilogram which were removed from the vault at the Bureau's Washington, D.C., site. At left is Dr. A. V. Astin, NBS Director, and on the right is A. G. McNish, Chief of the Bureau's Metrology Division. Witnessing the ceremony (background) are some of the winners of the 25th Annual Westinghouse Science Talent Search.

BRTHDAY

Seen through the glass window in the vault at Gaithersburg, along with the national standard of mass, the kilogram (under glass jars at right), are A. G. McNish, Dr. A. V. Astin, Dr. J. Herbert Hollomon, and Dr. Donald Hornig.

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in 1889 to serve as the U.S. standards for length and mass. They were fabricated in France under the agreement, called the Treaty of the Meter, which tied together the measurement systems of 20 nations (now 40). President Harrison personally accepted the meter bar and kilogram for this country. In 1901, they were placed in the custody of the newly created National Bureau of Standards, and in 1903, moved with NBS into its Connecticut Avenue site. So valuable and delicate are these two standards that even during their long stay in the vault at the Connecticut Avenue campus they were taken out less than once a year, usually to check the values of some lesser standards or to be checked themselves against the world standards kept in Paris. The kilogram standard has been back to Paris only twice and the meter bar four times since 1889.

Electromotive Series for

SOLID AND MOLTEN OXIDES AND HALIDES

Certain reactions at high temperature can now be more conveniently predicted since relative chemical activity scales of solid and molten halides have been prepared by W. J. Hamer of the NBS Institute for Basic Standards. A supplementary series of the relative chemical activity of solid and molten oxides permits the user to predict also whether the atmosphere will affect the reaction.[1]

Molten halides and oxides are already widely used in industry. In addition, they have promising potential applications as fuels or coolants in nuclear reactors and as electrolytes in fuel cells. In industry, molten salts are utilized in metallurgical processes to extract metals from ores, to descale or plate metal surfaces, and to determine metal corrosion rates at high temperatures. The solid halides and oxides are used as electrolytes in batteries in which extreme stability is necessary. Such batteries, which draw negligible current, are used as voltage standards and as grid bias batteries.

The NBS series for solid and molten halides and oxides have been developed for temperatures from 25 to 3000 °C based on the free energy of formation of the electrolyte phase and the heat capacities of the elements (electrodes) in the electrolyte phase. The fluoride, chloride, bromide, and iodide series cover 69, 96, 90, and 82 elements respectively. The elements are arranged in order of reducing power. The order of the elements, however, is not the same in the four series, so that relative reducing power may differ from one series to another. (For example, if lithium metal were placed in molten barium fluoride, it would displace the barium with the formation of lithium fluoride. However, in molten bromides or iodides, the reverse occurs.)

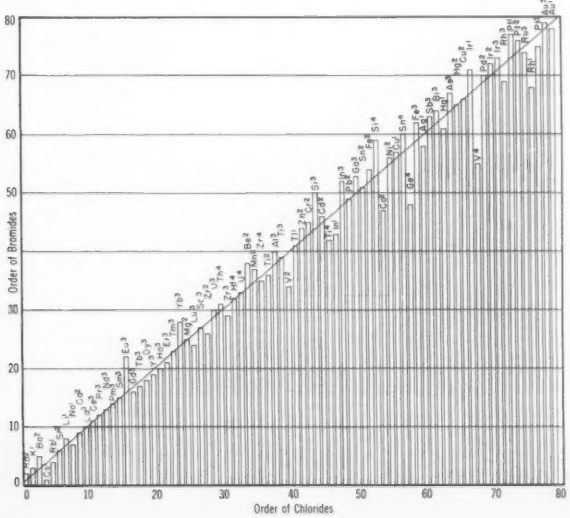
Along with each halide and oxide emf series, the emf of the corresponding aqueous solution is listed for comparison. The aqueous emf is the familiar electromotive series of relative reducing power listed in chemistry textbooks. Comparison of the order, according to increasing emf, of the molten and aqueous series, shows no agreement between the two series.

As an indication of the order of emfs (voltages) involved, the values for a selected number of elements in halides and oxides at 1000 °C are given in the table that follows:

	Fluorides	Chlorides	Bromides	Iodides	Oxides (s)
	Volts	Volts	Volts	Volts	Volts
Potassium (1)*	4.355 s	3.412	2.904	2.387	0.805 s
Cesium (1)	4.055 s	3.078	2.903	2.500	
Sodium (1)	4.529 s	3.019	2.667	2.135	1.256
Magnesium (2)	4.567 s	2.346	1.980	1.353 v	2.366 s
Manganese (2)	3.289 s	1.725	1.334	0.890 v	1.515 s
Cadmium (2)	2.605 s	1.002	0.876 v	(v)	0.538 s
Lead (2)	2.525 s	1.039 v	0.823 v	0.504 v	0.505
Iron (2)	2.780 s	1.050	0.730 v	0.295 v	0.920 s
Cobalt (2)	2.631 s	0.900	0.635 v	0.219 v	0.676
Copper (1)		0.943	0.605	0.324	0.400
Silver (1)	1.551	0.784	0.659	0.496	
Rhodium (3)	1.424 s	0.020 d	(d)	(d)	−0.138

*Number in parentheses is the valence of element in electrolyte.
s=solid; d=decomposes; v=volatile.

The electrochemical series of solid or liquid chlorides is compared to that of the bromides at 25 °C. The chlorides increase in activity from left to right, while the bromides increase with column height.



The data show that, in general, the electromotive force for any one element in the fluoride, bromide, chloride, and iodide series decreases as the atomic weight of the halide increases while the electromotive force of the corresponding element in the oxide series is in some cases higher and and some cases lower than the heaviest halide (iodide).

[1] For further details, see **Theoretical electromotive forces for cells containing a single solid or molten fluoride, bromide, or iodide,** by Walter J. Hamer, Marjorie S. Malmberg, and Bernard Rubin, J. Electrochem. Soc. **112**, 750 (1965), and **Theoretical electromotive forces for cells containing a single solid or molten oxide,** by Walter J. Hamer, J. Electroanalytical Chemistry **10**, 140 (1965); for earlier data on chlorides, see **Theoretical electromotive forces for cells containing a single solid or molten chloride electrolyte,** by Walter J. Hamer, Marjorie S. Malmberg, and Bernard Rubin, J. Electrochem. Soc. **103**, 8 (1956), and Electromotive series for solid and **molten chlorides,** NBS Tech. News Bull. **40**, 74 (1956).

Dr. W. Murray Bullis examines an oscilloscopic presentation of the characteristic of a sample of semiconductor material contained in the dark drum, above.

Semiconductor Flaw Study Initiated

Scientists of the electron devices laboratories of the NBS Institute for Applied Technology have embarked on an investigation of defects in semiconductor materials, in order to help industry produce more reliable devices. The Institute is undertaking this program on the recommendation of the Committee on Materials for Electron Devices and Microelectronics of the American Society for Testing and Materials.

The materials being studied in this long-range program are silicon and germanium. They are essential in the fabrication of transistors and diodes which are now coming to be more widely used in radios and "hi-fi's," as well as in more specialized electronic assemblies. Reliability of these semiconductor components, and of the more sophisticated integrated circuits using the same materials, is essential to modern scientific instrumentation, modern weaponry, and the communications systems for our national security and space programs.

The new program is under the direction of W. Murray Bullis, who came to NBS especially to conduct this investigation. Dr. Bullis' experience in semiconductor research, from his doctoral study of galvanomagnetic properties of germanium to his subsequent studies of other semiconductor properties during 8 years in the semiconductor industry, will be an asset to the Institute's investigations in this field.

The performance of transistors is determined to a great extent by minute differences in the composition, structure, and processing of the silicon and germanium. Flaws in these materials, usually resulting from chemical impurities or crystallographic defects, affect the electrical characteristics of circuits and devices.

The Institute's extensive program will include detecting and characterizing flaws and their effects on operation. This may in turn necessitate the development of new measuring techniques and will certainly require the use of increased precision in test procedures. The Institute scientists will work closely with their counterparts in industry, studying each step in the manufacturing process to seek the origin of flaws and their prevention. The material specifications and processing procedures that develop from this program are expected to be of assistance to industry in producing semiconductor materials and electron devices of more uniform quality.

ASTIN ELECTED TO AAAS POST

NBS Director A. V. Astin has been elected Vice President for Physics and Chairman of the Section Committee on Physics of the American Association for the Advancement of Science for 1966. As Vice President for Physics, Dr. Astin will also serve as a member of the AAAS Council—the Association's advisory and legislative body.

As Chairman of the Physics Section, Dr. Astin will be instrumental in planning activities and scientific sessions for the physicists who meet at the AAAS annual meeting to be held in Washington, D.C., December 26–31, 1966. The Bureau has a great deal of experience in planning and conducting scientific meetings; under Dr. Astin's direction, NBS can be expected to provide many services to the AAAS.

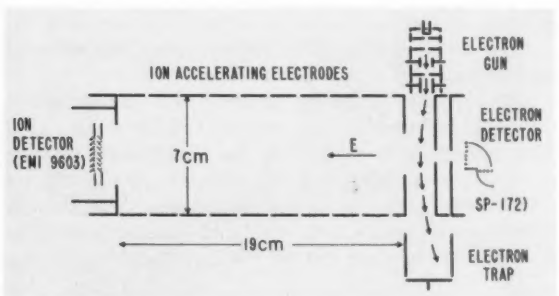
DECOMPOSITION OF MULTIPLY CHARGED IONS

New Technique Permits Direct Observation

A technique that provides direct experimental observation of multiply-charged ion decomposition has been developed [1] by K. E. McCulloh, T. E. Sharp, and H. M. Rosenstock of the NBS Institute for Basic Standards. The work was carried out with a coincidence time-of-flight mass spectrometer that permitted the simultaneous detection and mass analysis of singly charged fragments arising from the decomposition of multiply charged ions. While simultaneous detection and analysis of several particles is a well-known technique in nuclear physics, use of this approach in chemical problems is believed to be new.

Certain fragment ions in the mass spectra of molecules are known to form with unusually high kinetic energies of several electron volts, and numerous attempts have been made to identify their origin. Various suggestions have been made concerning these species, but all supporting evidence has been circumstantial. Methods of investigation based on conventional mass spectrometry encountered difficulty when decompositions of more than two fragments of highly different mass occurred. The present study shows that decomposition of multiply charged ions is the source of a substantial fraction of these fragments. This information will be of value in learning more about ionization phenomena.

The study was conducted with gases that were ionized by a 1-keV electron beam in the source area of the coincidence apparatus. The newly formed electrons and ions are accelerated in opposite directions by an electrostatic field defined by a series of ring electrodes. The ejected electrons fall through a potential of 450 volts and several vertical-defining slots and then strike the first dynode of a 14-stage electron multiplier. The positive ions are accelerated in the opposite direction through a horizontal-deflection slot and then strike an ion-electron multiplier. The apparatus is desinged so that the ions have a much greater distance to travel than do the electrons.



Schematic diagram of coincidence time-of-flight apparatus used at NBS to observe the decomposition of multiply charged ions into singly charged fragments. E indicates the direction of the electric field.

Ionization events are recorded as fast (about 10 nsec) pulses from the electron multipliers collecting the ejected electrons and positive ions. A single ionization is marked by a pulse from the ion detector which follows a pulse from the ejected-electron detector. The time interval between pulses is equal to the difference of travel times of these particles. Because of their greater masses and longer flight paths, ions have much longer travel times (525 nsec for protons) than do the ejected electrons (approximately 5 nsec).

Pulses from the ejected-electron multiplier and the ion multiplier are amplified and introduced into separate channels of a solid state coincidence time analyzer. The ejected electron pulse is then electronically delayed for a predetermined period of time and brought into coincidence with the ion pulse. The simultaneous appearance of the ion pulse and the delayed electron pulse will register a single ionization event.

This count is used as a reference. Throughout a long counting period the number of single ionization events may fluctuate, but the ratio of single ionization events to double ionization decomposition events should remain roughly constant.

Positive ion pairs that result from decomposition of doubly charged ions are registered by a different portion of the solid state counting apparatus. As the ion pairs have different masses, they can be separately detected by the mass spectrometer. The pulse due to the ejected electron (or electrons) is directed simultaneously into two delay channels; the first is designed to bring the pulse into coincidence with the heavier, slower ion, and the second is a shorter delay designed to bring the pulse into coin-

TABLE 1. *Observed positive ion pairs from various molecules* [a]

PARENT MOLECULE	PAIR TYPE	PARENT MOLECULE	PAIR TYPE
CO_2	$O^+ + CO^+$	CF_4	$F^+ + CF_3^+$
	$C^+ + O^+$		$F^+ + CF_2^+$
Propylene	$H^+ + C_1$		$F^+ + CF^+$
	$H^+ + C_2$	CH_4	$H^+ + CH_3^+$
	$H^+ + C_3$		$H^+ + CH_2^+$
	$H_2^+ + C_1$		$H^+ + CH^+$
	$H_2^+ + C_3$		$H^+ + C^+$
	$H_2^+ + C_3$		$H_2^+ + CH_2^+$
	$C_1 + C_2$		

[a] C_1, C_2, and C_3 represent unresolved groups of ions containing one, two, and three carbon atoms, respectively.

cidence with the lighter ion. Through an electronic gating system, an event will be registered only when coincidence is achieved in both cases. The system will reject pulses from incomplete situations where only one ion is in coincidence with the ejected electron pulse.

Mass analysis of ion pairs is accomplished by established time-of-flight mass spectrometer techniques. Charge-to-mass ratios of ions are determined by measuring the time required for an ion of given kinetic energy to travel a known distance from the source area to the ion detector.

This technique was applied to multiple ionization and fragmentation of carbon dioxide, carbon tetrafluoride, methane, and propylene. The results show positive ion pairs to be an important fraction of the fragment ions having high kinetic energy, and a large fraction of the products of double ionization. Significant yields of high-kinetic-energy protons and H_2^+ from such processes were observed for both methane and propylene.

[1] For further technical details, see Direct observation of the decomposition of multiply charged ions into singly charged fragments, by K. E. McCulloh, T. E. Sharp, and H. M. Rosenstock, J. Chem. Phys. **42**, 3501 (May 15, 1965).

STANDARDS AND CALIBRATION

IMMITTANCE QUESTIONNAIRE REPLIES

Last summer the High Frequency Calibration Services Section of the NBS Radio Standards Laboratory (Boulder, Colorado) sent out questionnaires to obtain estimates of the need for certain types of immittance calibrations. The questionnaires went to about 700 individuals and organizations who are presently using, or might in the future reasonably be expected to use, the NBS immittance calibration services. These services could be improved significantly, but at considerable expense, and it was therefore necessary to find out the degree of need.

The immittance calibrations dealt with in the questionnaire are divided into categories A, B, and C, each covering particular ranges of frequency (f), resistance (R), and inductance (L), in the following way:

A: f=10–350 kHz, R=0.02–1000 ohms, L=0.2–1000 μH

B: f=350–1 MHz, R=0.002–100 ohms, L=0.02–100 μH

C: f=1–10 MHz, R=0.0002–10 ohms, L=0.002–10 μH

SUMMARY			
Number of organizations requesting services	A: 46	B: 38	C: 40
Number of items to be submitted per year	A: 274	B: 204	C: 200

Replies were received from 198 organizations. In preparing the above summary, it was assumed that lack of a reply indicated satisfaction with existing services.

At present, services are offered in categories A and B, though at accuracies that some consider lower than desirable. On the other hand, there are no services in category C at all. The decision has therefore been taken, partly on the basis of the questionnaire, to design and prepare equipment for calibrations in category C at a reasonably high level of accuracy, the services to be made available in about a year. After that, attention will turn to categories A and B, and steps taken to upgrade their accuracy to about the same level as in category C.

SCALE EXECUTIVES MEET AT NBS

Over fifty top level representatives of scale manufacturers and scale service agencies, gathered at the NBS Gaithersburg site January 19–20 for a National Scale Conference sponsored jointly by NBS and the Scale Manufacturers Association. The main purpose of the seminar was to update participants on weights and measures laws, regulations, and methods of inspection and regulatory control. Discussions were based on the latest edition of NBS Handbook 44, which presents an entirely new approach to the technical requirements for weighing and measuring devices used in commerce.[1]

[1] NBS Handbook 44, Specifications, Tolerances, and Other Technical Requirements for Commercial Weighing and Measuring Devices, 3rd edition, issued Oct. 12, 1965. For sale at $2.00 per copy by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.

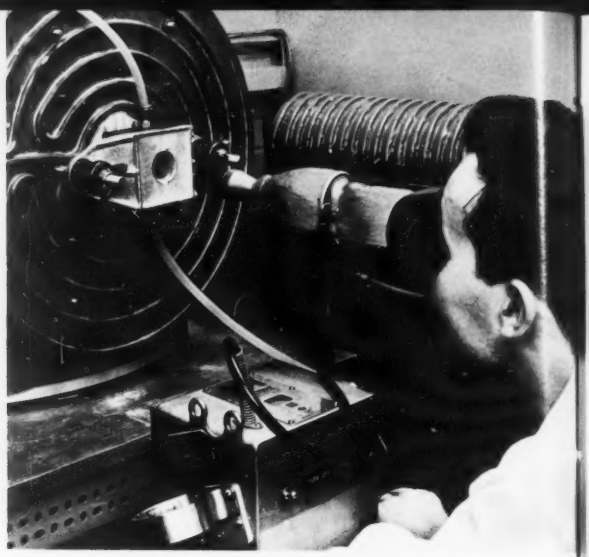
NOTICE OF U.S. STANDARD FREQUENCY AND TIME BROADCASTS

In accordance with Bureau policy of giving monthly notices regarding changes of phases in seconds pulses, notice is hereby given that there was no change in the phase of seconds pulses emitted from radio station WWVB, Fort Collins, Colo., on April 1, 1966.

Notice is also hereby given that there was no change in the phase of time pulses emitted from radio station WWV, Greenbelt, Md., and WWVH, Maui, Hawaii, on April 1, 1966. These pulses at present occur at intervals which are longer than 1 second by 300 parts in 10^{10}. This is due to the offset maintained in frequency, as coordinated by the Bureau International de l'Heure.

NEW THERMOCOUPLE TABLES

- *Wide Range*
- *High Temperature*



John S. Gallagher checks the temperature of a thermocouple in the NBS silicon carbide tube furnace to obtain data used in the computation of reference tables for the 30–6 thermocouple.

Research laboratories, glass manufacturers, steel plants and other metal industries, are finding an increased need for precision measurement of temperature in the 1300 to 1800 °C range. Recently many of these concerns have found that a new thermocouple, of platinum-30 percent rhodium versus platinum-6 percent rhodium, provides a reliable measuring device at these temperatures. The "30–6 thermocouple" is designed primarily for use at the higher temperatures (1300 to 1800 °C) and, in addition to its high operating temperature, has the advantage of high stability, good mechanical strength, and wide range.

To facilitate calibration and use, the NBS Institute for Basic Standards, at the request of the American Society for Testing and Materials, has developed reference tables [1] for the new thermocouple. George W. Burns and John S. Gallagher prepared the tables by calibrating 11 thermocouples from 4 manufacturers (3 American and 1 European). The temperature-emf relationship given by these tables is believed to be representative of materials now being produced in this country.

The thermocouples were calibrated from 0 to 1100 °C using a nickel-chromium tube furnace for heating and a platinum versus platinum-10 percent rhodium thermocouple for temperature reference. In the 1050 to 1600 °C range the thermocouples were heated by a silicon carbide tube furnace and calibrated by direct comparison with an optical pyrometer. In addition, the thermocouples were calibrated by comparison with a platinum versus platinum-10 percent rhodium thermocouple from 1063 to 1450 °C. To insure greater accuracy they were heated in a platinum-rhodium wire wound furnace and calibrated from 1063 to 1790 °C by direct comparison with an optical pyrometer.

With the use of a digital computer, equations were fitted by the method of least squares to the sets of emf-temperature values obtained for each thermocouple. After plotting these emf-temperature curves for all thermocouples, a representative curve was drawn by visually estimating the best fit. Values were taken from this curve at 25-deg intervals from 0 to 1825 °C. It was found that a curve passing through these points could be represented by 3 polynomial equations. From these equations the tables were generated by the digital computer.

The reference tables thus obtained provide a basis for the accurate calibration of 30–6 thermocouples throughout science and industry. Tests at NBS have shown that calibration of any 30–6 thermocouple at four points (about 600, 1063, 1300, and 1552 °C) is sufficient to construct a deviation curve from the reference tables such that the resulting calibration will be accurate to within ±6 microvolts up to 1063 °C, the equivalent of about ±3 °C up to 1552 °C, and the equivalent of about ±5 °C above this temperature. Calibration values at the higher temperatures may be obtained accurately by extrapolation.

Tests have also shown the thermocouple must have proper insulation and protection to remain stable at high temperatures. High purity alumina with low iron content is recommended for this protection.

[1] See Reference tables for the Pt-30 percent Rh Vs Pt-6 percent Rh thermocouple, by George W. Burns and John S. Gallagher, J. Res. NBS 70C (Engr. and Instr.) (April–June 1966).

PUBLICATIONS *of the National Bureau of Standards**

PERIODICALS

Technical News Bulletin, Volume **50**, No. 4, April 1966. 15 cents. Annual subscription: $1.50. 75 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis.

Journal of Research of the National Bureau of Standards:

Section A. Physics and Chemistry. Issued six times a year. Annual subscription: Domestic, $5; foreign, $6. Single copy, $1.00.

Section B. Mathematics and Mathematical Physics. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75. Single copy, 75 cents.

Section C. Engineering and Instrumentation. Issued quarterly. Annual subscription: Domestic, $2.75; foreign, $3.50. Single copy, 75 cents.

CURRENT ISSUES OF THE JOURNAL OF RESEARCH

J. Res. NBS **70A** (Phys. and Chem.), No. 3 (May–June 1966).

Thermal relaxation and Brillouin scattering in liquids. R. D. Mountain.

Density of polyethylene crystals grown from solution. G. M. Martin and E. Passaglia.

Mechanical relaxation in polyethylene crystallized with various degrees of lamellar orientation. J. M. Crissman and E. Passaglia.

Pentafluorophenyl alkyl and vinyl ethers. W. J. Pummer and L. A. Wall.

Calibration of germanium resistors at low temperatures (2–20° Kelvin). G. Cataland and H. H. Plumb.

Dissociation pressure of aluminum carbide using a rotating Knudsen cell. E. R. Plante and C. H. Schreyer.

Determination of intermolecular potential functions from macroscopic measurements. M. Klein.

J. Res. NBS **70C** (Engr. and Instr.), No. 2 (Apr.–June 1966).

Design and statistical procedures for the evaluation of an automatic gamma-ray point-source calibrator. S. B. Garfinkel, W. B. Mann, and W. J. Youden.

Testing of lenses with the wave front reversing interferometer. K. Muraoka.

Ellipsoidal mirror reflectometer. S. T. Dunn, J. C. Richmond, and J. A. Wiebelt.

Reference tables for the Pt-30 percent Rh versus Pt-6 percent Rh thermocouple. G. W. Burns and J. S. Gallagher.

Coaxial power meter calibration using a waveguide standard. G. F. Engen.

A note on the numerical evaluation of thermal radiation characteristics of diffuse cylindrical and conical cavities. B. A. Peavy.

OTHER NBS PUBLICATIONS

Copper wire tables, NBS Handb. 100 (Feb. 21, 1966). 50 cents. Supersedes Circular 31.

Procedures for precise determination of thermal radiation properties, November 1963 to October 1964, J. C. Richmond, S. T. Dunn, D. P. DeWitt, and W. D. Hayes, Jr., NBS Tech. Note 267 (Dec. 17, 1965). 45 cents.

Earth's field static calibrator for accelerometers, P. S. Lederer and J. S. Hilten, NBS Tech. Note 269 (Feb. 1, 1966). 20 cents.

An outline for cooperative action on the determination of x-ray mass attenuation coefficients in the wavelength range from 0.5 to 100 Å (25 to 0.12 keV), K. F. J. Heinrich, NBS Tech. Note 284 (Feb. 21, 1966). 15 cents.

Computation of the permeability and permitivity of a relatively small ring sample in a toroidal coil, E. G. Johnson, Jr., NBS Tech. Note 311 (Jan. 25, 1966). 30 cents.

An atlas of solar flare effects in the ionosphere observed with a high-frequency Doppler technique, September 1960–December 1962, D. M. Baker, NBS Tech. Note 326 (Dec. 1, 1965). 60 cents. (Formerly the Central Radio Propagation Laboratory of the National Bureau of Standards, now Environmental Science Services Administration, Boulder, Colo.)

The seasonal variation of nightglow NaI 5890–96 A, [01] 5577 A and [01] 6300 A in the tropics, L. L. Smith and R. W. Owen, NBS Tech. Note 329 (Jan. 10, 1966). 35 cents. (Formerly the Central Radio Propagation Laboratory of the National Bureau of Standards, now Environmental Science Services Administration, Boulder, Colo.)

Computations of the antenna cut-back factor for LF radio waves, D. C. Hyovalti, NBS Tech. Note 330 (Nov. 26, 1965). 30 cents. (Formerly Central Radio Propagation Laboratory of the National Bureau of Standards, now Environmental Science Services Administration, Boulder, Colo.)

A 100 KW 2–25 Mc/s distributed amplifier, designed for use with 10 KW ionospheric sounders, W. B. Harding, M. W. Woodward, and J. C. Carroll, NBS Tech. Note 331 (Feb. 15, 1966). 20 cents. (Formerly Central Radio Propagation Laboratory of the National Bureau of Standards, now Environmental Science Services Administration, Boulder, Colo.)

PUBLICATIONS IN OTHER JOURNALS

This column lists all publications by the NBS staff, as soon after issuance as practical. For completeness, earlier references not previously reported may be included from time to time.

Chemistry

A review of zinc oxide-eugenol type filling materials and cements, G. M. Brauer, Rev. Belge. Med. Dent.-Belg. Tijds. Tandheelk **20**, No. 3, 323–364 (1965).

Application of a high-intensity, multi-slit Raleigh interferometer to sedimentation studies, I. H. Billick and R. J. Bowen, J. Phys. Chem. **69**, 4024–4030 (1965).

Crystal and molecular structure of $C_4B_{20}H_{22}$, bis (*o*-dodecacarborane), L. H. Hall, A. Perloff, F. A. Mauer, and S. Block, J. Chem. Phys. **43**, No. 11, 3911–3917 (Dec. 1965).

Dissociation of ammonium ion in methanol-water solvents, M. Paabo, R. G. Bates, and R. A. Robinson, J. Phys. Chem. **70**, No. 1, 247–251 (1966).

Electrochemistry, W. J. Hamer, Book, Encyclopedia of Physics, pp. 200–203 (Reinhold Publ. Corp., New York, N.Y., 1966).

Kinetics of the hydroxyl radical in aqueous solution, F. Sicilio, R. E. Florin, and L. A. Wall, J. Phys. Chem. **70**, No. 47, 47–52 (Jan. 1966).

Manganese-hydrogen bond distance in $HMn(CO)_5$, T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, J. Am. Chem. Soc. **88**, 184 (Jan. 5, 1966).

Matrix-isolation infrared spectrum of the free radical CCO, M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. **43**, No. 10, 3734–3746 (Nov. 1965).

Matrix-isolation infrared spectrum of the free radical NH_2, D. E. Milligan and M. E. Jacox, J. Chem. Phys. **43**, No. 12, 3487–4493 (Dec. 15, 1965).

**Publications for which a price is indicated are available by purchase from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402 (foreign postage, one-fourth additional). The NBS nonperiodical series are also available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 22151. Reprints from outside journals and the NBS Journal of Research may often be obtained directly from the authors.*

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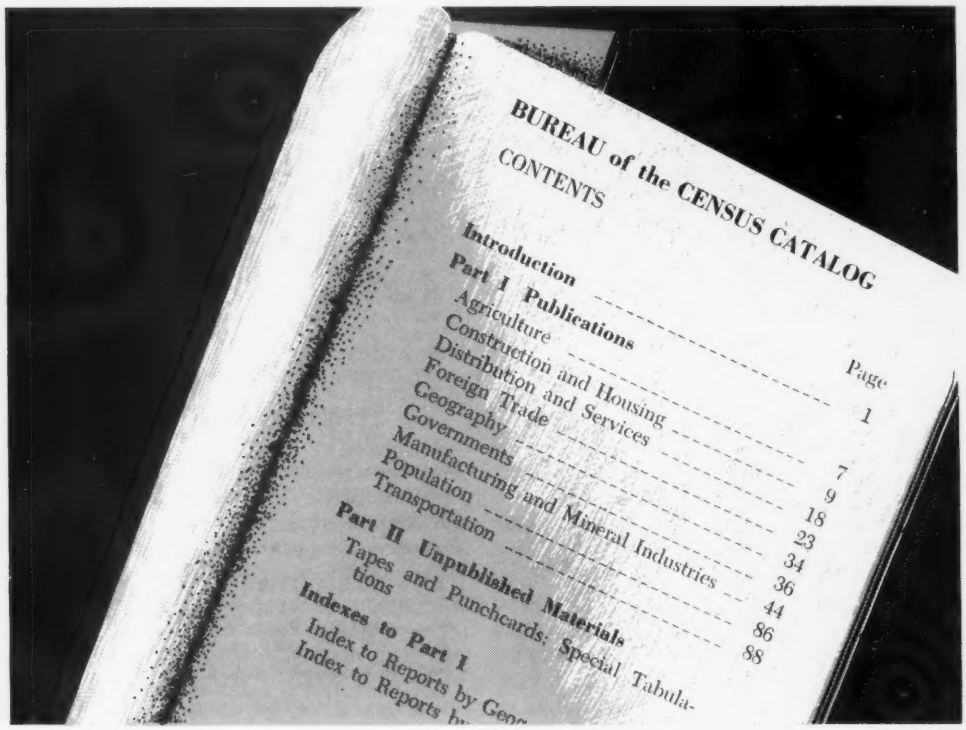

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